Fundamental Studies of NOx Adsorber Materials

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Institute for Interfacial Catalysis
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CLEERS WORKSHOP 8
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Funding – DOE/OFCVT
Studies Performed to Date

- **Studies of Ba loading:**
  - Morphology of the BaO storage material
  - Optimum morphology
  - Need for ‘contact’ with Pt?
  - What limits time to initial NOx ‘breakthrough’?

- **Variation of catalyst preparation:**
  - Can time to ‘breakthrough’ be extended?

- **Catalyst composition:**
  - Variation in the storage material – BaO, CaO, SrO, MgO
  - Variation in the support material – acidic, basic, ‘neutral’

- **Mechanistic studies:**
  - Reductive regeneration: nitrogen-balance experiments with production catalysts
  - NO oxidation: Pt particle-size dependence and deactivation
Methods

- **Synchrotron Temperature Programmed-XRD**: catalyst structural changes *(with Jon Hanson NSLS/Brookhaven National Lab)*
- **Transmission electron microscopy (TEM/EDX)**: morphological changes
- **FTIR and NMR Spectroscopies, and Temperature-programmed desorption (TPD)**: surface chemistry
- **Lab Reactor**: performance measurements, kinetics and mechanisms
Evolution of LNT material morphology during preparation and use.

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Will very briefly show select pieces of data from these studies.
Quantification of NOx uptake reveals small percentage of BaO used for storage

250 °C

Assume $\text{Ba(NO}_3\text{)}_2$ formation

Why so little?
Calcination of 20%-BaO/Al$_2$O$_3$: TP-XRD

- Ba(NO$_3$)$_2$ completely decomposes at ~575 °C
- Weak BaO lines form (nano particle formation)

Experiments performed at the National Synchrotron Light Source in collaboration with Jon Hanson, Brookhaven National Laboratory
Ba(NO$_3$)$_2$ decomposition on Al$_2$O$_3$: TP-XRD

Integrated area (11.6°, a.u.)

Intensity

Temperature (°C)

2Theta (°)

Particle size (Å)

<particle size>~62nm

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20%-BaO/Al$_2$O$_3$, Calcined at 500 °C: TEM and EDS

Well dispersed BaO particles all over the Al$_2$O$_3$ support surface.

EDS (Atomic%)
Al:83  Ba:17
82  18
The morphology of BaO/Al$_2$O$_3$ as synthesized

Large Ba(NO$_3$)$_2$ crystallites

BaO nanoparticles on a BaO monolayer
Lean-NOx Trap (LNT) morphology changes shown in this ‘movie’ are based on the results of combined transmission electron microscopy (TEM), temperature-programmed desorption (TPD), FTIR and NMR spectroscopy, and synchrotron TP-XRD experiments.
NO and NO$_2$ Desorption From BaO/Al$_2$O$_3$ Following NO$_2$ Adsorption at 300K

Signatures of two ‘forms’ of nitrate?


By combining FTIR and NO$_2$ TPD:

- **420 °C**: decomposition of bidentate nitrates
  \[ \text{Ba(NO}_3\text{)}_2 \rightarrow \text{BaO} + 2\text{NO}_2 + \frac{1}{2}\text{O}_2 \]

- **500 °C**: decomposition of ionic nitrates
  \[ \text{Ba(NO}_3\text{)}_2 \rightarrow \text{BaO} + 2\text{NO} + \frac{3}{2}\text{O}_2 \]
Distribution of NO and NO$_2$ Desorption Features Very Sensitive to BaO Loading

- $\text{Al}_2\text{O}_3$: bidentate nitrates
- 2%-BaO/$\text{Al}_2\text{O}_3$: bidentate nitrates (BN)
- 8%-BaO/$\text{Al}_2\text{O}_3$: bidentate nitrates (BN) + ionic nitrates (IN) [BN$>$IN] (very little NO$_2$ adsorption on BaO-free $\text{Al}_2\text{O}_3$)
- 20%-BaO/$\text{Al}_2\text{O}_3$: bidentate and ionic nitrates [BN$<$IN] (virtually no $\text{Al}_2\text{O}_3$ surface is BaO-free)
Nitric oxide (NO) and nitric oxide (NO₂) adsorption on 8%- and 20%-BaO/Al₂O₃ catalysts at 300K.

Ionic (IN) (bulk) and bridging (BN) (surface) nitrates are observed on both BaO/Al₂O₃ catalysts. The ratio of bridging/ionic nitrates varies with BaO loading. (Al₂O₃-bound nitrates (AN) are also present.)
NO$_2$ and NO$_2$+H$_2$O on BaO/Al$_2$O$_3$: 
$^{15}$N Solid State NMR

Three types of nitrates:
- on alumina (easily removed by H$_2$O);
- Surface nitrates (peak sharpens with H$_2$O addition);
- bulk-like nitrates (unchanged by H$_2$O addition)
Heat

NO + \( \frac{1}{2} \) O

Ba(NO\textsubscript{3})\textsubscript{2} \\

Al\textsubscript{2}O\textsubscript{3}

Heat

ionic Nitrates (bulk)

Bridging Nitrates (Surface)

Ba(NO\textsubscript{3})\textsubscript{2} \\

Al\textsubscript{2}O\textsubscript{3} \\

\( \text{BaO} \) \\

\( \text{Al}_2\text{O}_3 \)
While SO₂ monotonically decreased the desorption from ‘bulk’ nitrates, NO₂ adsorption on ‘monolayer’ nitrates is unaffected at low sulfur levels. In a similar way, performance degradation is minimal at low sulfur exposures but progresses rapidly once begun.
Mechanistic Studies During Rich Regeneration: Nitrogen-Balance Experiments

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Experimental Details

- Quartz reactor: 1”OD x 7/8” id; Temp. control via programmable furnace
- FTIR: 2 meter, 200 cc cell at 50 °C, 1 atm
  --- NO, NO₂, N₂O, NH₃, CO, CO₂, H₂O ....
  Repeat time as fast as 2 seconds
- Micro GC with 3 independent columns;
  Used for detection of N₂, O₂ and H₂
  10-20 lean-rich cycles needed to collect GC data
- Chemiluminescent NOx Analyzer

Standard Gases: 280 ppm NO
10% CO₂
0 – 25 ppm SO₂ (to date, none used)
0-2% H₂O (to date, none used)

Lean Phase: 4-8% O₂
Rich Phase: 4% CO or 1.3% H₂

Flow: 1-3 slm over (3-7 cc) catalyst brick – Space velocity: 8,000-50,000/Hr
3 way solenoid valves – lean and rich gas mixtures always flowing
Lean NOx Trap Catalysis System

O₂
He

He CO₂ NO SO₂ H₂O

H₂ CO C₃H₆ He

Exhaust

Bypass

Furnace

FTIR

2.5 liter Cyl.

Micro GC

CLA NOx

Exhaust

3 way Solenoid valves control lean/rich flows
Testing ‘Degreened’ UMICOR Monolith

Conditions:

2 SLM flow over 6.9 cc catalyst brick (2.08 cm long; 2.06 cm dia)
SV ~ 17000/Hr

Temperature ~250 °C

Gases: He + 280 ppm NO flowing at all times; 70 seconds lean: 4% O₂
Variable rich cycle (2-20 seconds): 1.3% H₂
No water added, but it is formed from H₂ oxidation during the rich cycle
Umicore GDI LNT: ORNL Elemental Screening Results

• Green
  – Washcoat:
    • Zr, Ce
    • La additive/impurity
  – Precious Metals:
    • Pt, Pd, Rh in descending concentration
  – Sorbate (Group I, II):
    • Ba major
    • Sr, Na detected as minors/impurities

• Degreened: 16 hrs, 700ºC
  – Washcoat:
    • Zr, Ce
    • La additive/impurity
  – Precious Metals:
    • Pt, Pd, Rh in descending concentration
  – Sorbate (Group I, II):
    • Ba major
    • Sr, K, Na detected as minors/impurities

Bottom Line: Umicore LNT chemistry is similar to Three-Way Catalyst with Barium for NOx storage
Waited until consistent results were obtained in FTIR data
Example ‘steady-state’ data

3 Seconds Rich

NO  N2O  NO2  NH3

Time

Example Example ‘steadystate’ data
3-second rich period insufficient to regenerate LNT

- No NH$_3$ formation
- N$_2$O formed early in the rich cycle
- Significant NOx (NO and NO$_2$) ‘puffs’ when cycled rich
~6-8 second rich period optimum for regeneration

- No NOx (NO and NO₂) breakthrough!
- N₂O formed early in the rich cycle
- Small amount of NH₃ formation late in the cycle
Longer rich periods result in significant NH$_3$ formation.
N$_2$ readily detected and quantified by GC

3 Seconds Rich

FWHM ~2.7 Seconds

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\( \text{N}_2 \) formation occurs early in the rich cycle, before \( \text{NH}_3 \)
$N_2$ formation maximizes at ~5-6 seconds

N2 Data; 2 to 20 s Rich/66 Lean
2slm; 6.9 cc degr. UMICOR Monolith
4%O2; 1.3%H2; 280 ppm NO; 250 C
Nitrogen balance > 90%

- NOx conversion reaches 90% for 6 seconds.
- NH$_3$ only becomes a significant product more rich times > 8s.
- N$_2$O ~5-10% of NO-in and insensitive to rich time.
- Reductant (H$_2$) breakthrough at >10 s rich.

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<th>Catalyst Out</th>
<th>Seconds Rich</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>10</th>
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<td>3</td>
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<td>% NO in</td>
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<td>0.2</td>
<td>0.4</td>
<td>0.1</td>
<td>0.6</td>
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<td>1.7</td>
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<td>Sum % Nox Converted</td>
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<td>63.9</td>
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<td>97.1</td>
<td>94.9</td>
<td>97.6</td>
<td>103.9</td>
<td>98.5</td>
<td>94.7</td>
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<td>% N recovered</td>
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<td>93</td>
<td>96</td>
<td>94</td>
<td>98</td>
<td>95</td>
<td>98</td>
<td>104</td>
<td>99</td>
<td>95</td>
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<td>H$_2$O ppm-sec</td>
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<td>52680</td>
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<td>% of total H$_2$ in</td>
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<td>112</td>
<td>101</td>
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<td>89</td>
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<td>0</td>
<td>7</td>
<td>36</td>
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</table>
Distribution of N-containing species with varying rich times

2-20_Sec_Nresults--%
Initial Experiments: Compare Product Distributions with $\text{H}_2$ versus CO

- Used 7.2 cc LNT brick (commercial LNT catalyst from a 2004 Ford Mondeo 1.8 SCI – obtained from John Hoard and George Graham, Ford Scientific Research Labs)
- 1 slm for ~ 18000/Hr over Catalyst at 210 °C
- Vary reductant — $\text{H}_2$ or CO
- Input 500 ppm NO, look for $\text{N}_2$
- Dropped $\text{O}_2$ to 2% for simpler $\text{N}_2$ detection
Nitrogen Balance, Third cycle

- Detected $N_2$ — 60% of NOx over cycle to $N_2$
- Late $NH_3$ production as $N_2$ production drops
- No NOx breakthrough during 'steady-state' reduction phase

<table>
<thead>
<tr>
<th>Lean</th>
<th>Rich</th>
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<tr>
<td>NOx in: 6123 ppm-min</td>
<td>NOx in: 6123 ppm-min</td>
</tr>
<tr>
<td>NO out: 253 ppm-min (4%)</td>
<td>NO out: 253 ppm-min (4%)</td>
</tr>
<tr>
<td>N2O out: 237 ppm-min (8%)</td>
<td>N2O out: 237 ppm-min (8%)</td>
</tr>
<tr>
<td>NH3 out: 942 ppm-min (15%)</td>
<td>NH3 out: 942 ppm-min (15%)</td>
</tr>
<tr>
<td>N2 out: 3694 ppm-min (60%)</td>
<td>N2 out: 3694 ppm-min (60%)</td>
</tr>
</tbody>
</table>

Overall: 88% N recovery

210C; 1slm 7.4cm$^2$~(8100/Hr); 480ppm NO in; 10%CO2; + He 2%O2/1.3%H2 lean/rich
Nitrogen Balance—Third Cycle

- Small N₂ signal—only spike on Rich-to-Lean transiton
- Much lower NOx conversion with CO vs H₂ as reductant

**Graph Details:**
- NOx in 6422 ppm-min
- NO out: 2755 (43%)
- NO₂ out: 43 (0.7%)
- N₂O out: 922 (29%)
- N₂ out: 357 (11%)

84% N recovery

**Conditions:**
- 210C; 1slm 7.4cm³~(8100/Hr)
- 480ppm NO in; 10%CO₂; + He
- 8%O₂/4%CO lean/rich

**Institute Logos:**
- Pacific Northwest National Laboratory
- Institute for Interfacial Catalysis
Summary and Conclusions

• The morphology of BaO/Al$_2$O$_3$ LNT materials is remarkably dynamic during NOx storage and reduction. A ‘monolayer’ of Ba(NO$_3$)$_2$ forms on the alumina surface in addition to large bulk Ba(NO$_3$)$_2$ particles.

• As the amount of barium oxide increases, the NOx uptake also increases. However, a significant fraction of the BaO sites (up to 80%) do not take part in the formation of Ba(NO$_3$)$_2$ even after uptake for extended periods.

• and NMR spectroscopies display features that correlate well with these two ‘forms’ of Ba(NO$_3$)$_2$. These two forms also appear to decompose in two distinct temperature regimes and give rise to two different desorption products.

• Early stages of sulfur adsorption appears to effect ‘bulk’ uptake first before ‘monolayer’ uptake.

• Nitrogen balance experiments show the distribution of N-containing products during rich regeneration. While N$_2$ and N$_2$O form early in the rich phase, extended rich periods lead to the production of significant quantities of NH$_3$. Marked differences are observed in the products produced during rich regeneration of production LNTs when comparing reduction by H$_2$ and CO.
Future Work

- **BaO morphology studies**
  - Effects of CO$_2$ and/or H$_2$O on morphology changes during NOx uptake and release. TP-XRD studies to be performed at National Synchrotron Light Source (NSLS) this summer.
  - In-situ TEM studies to watch morphology changes in real time.
  - Effects of additional catalyst components (e.g., ceria as used in CLEERS Umicore material), and alternative support materials (e.g., MgO and MgAl$_2$O$_4$).
  - Role of Pt/BaO interface for optimum NOx storage.

- **Studies of CLEERS Umicore samples**
  - CLEERS performance protocol experiments
  - Additional nitrogen balance experiments
    - Varying reductant (1 or more of H$_2$, CO, and/or C$_3$H$_6$)
    - Add in CO$_2$ and H$_2$O
    - Varying lean times
    - Varying temperatures